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Corrosion Resistance Study of Heat Treated 420 Martensitic Stainless Steel and 316 Austenitic Stainless Steel in Dilute Acid Concentrations

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Abstract
The corrosion resistance of quenched 420 martensitic and annealed 316 austenitic stainless steels were evaluated through coupon analysis, potentiodynamic polarization technique and optical microscopy in 1-6M H_2SO_4 and HCl acid media. Results show that the heat treated 316 stainless steel had a significantly higher corrosion rate than the 420 martensitic steel. Heat treatment greatly improved the corrosion resistance and passivation characteristics of the martensitic steel at all acid concentrations studied with an average percentage improvement of 62% and 56.2% in corrosion rate from H2SO4 and HCl acid. The heat treated austenitic steel showed limited change in corrosion resistance with an average percentage improvement of 30.9% and 29.25% in corrosion rate from H2SO4 and HCl acid. Micrographs from optical microscopy showed a less corroded morphology for martensitic steel in comparison to the austenitic steel due to the presence of retained austenite and martensite formation.

Key words: Corrosion; Heat Treatment; Passivation; Acid

1. INTRODUCTION

The foundation of modern industry is stainless steel due to its versatile application in aqueous corrosive environments in a significant number of industries (Khatak and Baldev, 2002; Oberndorfer *et al*., 2002) Advance manufacturing techniques and high volume production of stainless steels has resulted in the availability of cost effective and corrosion resistant steels (Marshall, 1984). Austenitic stainless steels grades generally have strong corrosion resistance in mildly corrosive acid, industrial and marine environments (Raymond and Higgins, 1985). Martensitic stainless steels have good mechanical properties and strong resistance to surface deterioration. They are used majorly in industries such as chemical processing plants, power generation devices and equipments, aerospace, oil and gas refineries and marine applications (Brickner, 1968). These grades are however susceptible to corrosion at slightly higher concentrations and in the presence of chloride ions, most especially to pitting corrosion (Dell, 1989; Betova *et al*., 2002).

Chromium and to a lesser extent nickel and molybdenum are the most important elements in the resistance and susceptibility of stainless steels to corrosion (Palit *et al*., 1993; Gaudett and Scully, 1994). Their resistance is determined by their passivation characteristics, elemental composition, heat treatment and the corrosive medium. The durability of the protective covering on stainless steels is subject to its self-healing ability (Fadare and Fadara, 2013; Kempester, 1984). The film collapses when the rate of corrosion is much faster than the reforming rate leading to severe localized corrosion attack and eventually catastrophic failures. Most research conclusions state that Cl- ions diffuses through the passive films causing its breakdown at the metal/film interface, (Dong and Zhou, 2000; Strehblow *et al*, 1995). Stimming (1986) showed in his work that the presence of hydrogen atoms within a passive film destroys the durability of the film, promotes its breakdown and hinders the repassivation process. The need for superior corrosion resistant properties in specific industrial applications necessitates performance improvement on the surface property and metallurgy of these steels (Millano *et al*., 2006; Aponte *et al*., 2008). Altering the microstructure of stainless steel significantly improves their corrosion resistance. Microstructural constituents such as grain size, phases, precipitates, flaws and inclusions are strongly modified by heat treatment to effect changes in their mechanical, chemical and surface properties based on the austenite/martensite formation, changes in grain size and defects (Rajan, 1998). Heat treatment through quenching involves cooling a metal rapidly to produce a martensite transformation (harder metal) after heating the metal above the upper critical temperature. Rapid cooling causes a part of the austenite to change to martensite. The hardness of a metal due to quenching is a product on its chemical constituent and quenching process.

Previous researches on the effect of heat treatment processes on the corrosion resistance of stainless steel have given mixed results. Lu *et al* (2015) studied the changes due to heat treatment on the microstructure characteristics and the electrochemical behaviour of plastic mold steel in chloride solution. Results showed that the corrosion resistance of the as-quenched martensitic steels increased with austenitizing temperature but decreased after tempering. Nasery *et al* (2011) studied the effects of astenitizing temperature, tempering temperature and time, and on the microstructure, mechanical and corrosion properties of AISI 420 martensitic steel. Results showed that the temperature significantly influenced the mechanical properties of the steel. The

corrosion parameters were not slightly influenced by increment of austenitizing temperature. The effects of heat treatment on microstructure, hardness uniformity, surface roughness and corrosion resistance of a 13Cr-type martensitic stainless steel was studied by means of optical microscopy, scanning and transmission electron microscopy and polarization resistance. Observation showed that the corrosion resistance of the steels reduced after tempering in comparison to quenching (Lu *et al*., 2015). Choi *et al* (2007) studied the relationship between different austenitizing temperature of 0.3C-14Cr-3Mo type stainless steel and their electrochemical performance in Cl^- containing neutral aqueous solutions. He observed that increase in austenitizing temperature caused a proportionate increase in corrosion and pitting potential of martensitic steel due to precipitation of fewer carbides among the steel matrix after high temperature austenitization. This research aims to study and compare the effect heat treatment (quenching) on the surface property and corrosion resistance of type 420 martensitic stainless steel and 316 austenitic stainless steel in specific concentrations of HCl and H_2SO_4 acid.

2. EXPERIMENTAL PROCEDURE

2. 1. Materials

420 martensitic stainless steel (MSS 420) and 316 austenitic stainless steels (ASS 316) obtained commercially and analyzed at the Materials Characterization Laboratory, Department of Mechanical Engineering, Covenant, Ogun State, Nigeria gave an average nominal composition of nominal per cent (%) composition shown as in Table 1.

Table 1. Percentage Nominal Composition of MSS 420 and ASS 316 stainless steel

	C	Mn	P	S	Si	Cr	Ni	Mb	N	Fe
MSS 420	0.28	0.8	0.04	0.02	0.75	13.5	0.4	-	-	79.15
ASS 316	0.07	0.04	0.03	0.05	0.75	18	10	2	0.2	68.86

2. 2. Acid test solution

Specific concentrations (1-6M) of dilute H_2SO_4 and HCl acid solution at 150 mL were prepared by dilution of an analytical grade of both acids (98% H_2SO_4 and 37% HCl) with distilled water and used as the corrosive test medium.

2. 3. Preparation and heat treatment of stainless steel samples

MSS 420 and ASS 316 stainless steel were machined into 6 test samples each for both steels with HSS parting tool on a lathe machine. The average length and diameter of the martensitic steel is 10 mm x 12 mm while the austenitic steel is 10 mm x 5 mm. The two exposed surface ends of the steel samples were metallographically prepared with silicon carbide abrasive papers of 80, 120, 220, 800 and 1000 grits before being polished with 6 µm diamond liquid, rinsed with distilled water and acetone, dried and later stored in a dessicator for weight-loss analysis and potentiodynamic polarization resistance technique in accordance with ASTM G1 - 03(2011). MSS 420 steel samples were heat treated in a muffle furnace above the transformation range to 1000^{o}C before being rapidly cooled in distilled water to achieve the desired metallurgical structure of hardened martensite while keeping distortion to a minimum. The temperature was regulated using a temperature regulator of accuracy ± 10°C coupled with thermocouple (K-Type) to give the actual sample temperature. ASS 316 steel samples were furnace heated to 1000^{o}C, maintained at the temperature for about 30 minutes and then slow cooled at a controlled temperature.

2. 4. Potentiodynamic polarization test

Potentiodynamic polarization was performed with the MSS 420 and ASS 316 stainless steel electrodes mounted in acrylic resin with an unconcealed surface area of 113.04 mm^2 and 19.6 mm^2 respectively. The steel electrode was prepared according to ASTM G59-97(2014). The polarization studies were performed at 25^{o}C ambient temperature with Digi-Ivy 2300 potentiostat and electrode cell containing 150 mL of the acid media. Platinum was used as the counter electrode and silver chloride electrode (Ag/AgCl) as the reference electrode. Potentiodynamic measurement was performed from -1.5V to +1.5 V at a scan rate of 0.0016 V/s according to ASTM G102-89(2015). The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) were calculated from the Tafel plots of potential versus log current. The corrosion rate (γ) and the percentage inhibition efficiency (η_2) were from equation 1.

$$\gamma = \frac{0.00327 \times J_{\mathrm{corr}} \times E_{\mathrm{q}}}{D} \quad (1)$$

where j_{corr} is the current density in µA/cm^2, D is the density in g/cm^3; E_q is the specimen equivalent weight in grams. 0.00327 is a constant for corrosion rate calculation in mm/y (Sethi *et al*., 2007; Ahmad, 2006).

2. 5. Coupon analysis

Weighed steel samples were individually immersed fully into 150 mL of the dilute acid media for 480 h at ambient temperature of 25 ^{o}C. Each sample was removed from the solution at 24 h interval, rinsed with distilled water and acetone, dried and re-weighed according to ASTM G31-12a (2012). Graphical illustrations of corrosion rate, $\mathfrak{r}$ (mm/y) and percentage inhibition efficiency (η) versus exposure time T were plotted from the data obtained during the exposure hours. The corrosion rate ($\mathfrak{r}$) calculation is defined as (Moussa *et al*., 2007)

$$\mathfrak{r} = \left[\frac{87.6\tilde{\omega}}{DAT}\right] \quad (2)$$

where $\tilde{\omega}$ is the weight loss in mg, D is the density in g/cm^3, A is the total area in cm^2 and 87.6 is a constant.

2. 6. Optical microscopy characterization

Optical micrographs of the surface morphology and topography of the heat treated stainless steel sample was studied after weight-loss analysis with the aid of Omax trinocular optical metallurgical microscope at the Physical Metallurgical Laboratory, Covenant University, Ogun state, Nigeria.

3. RESULTS AND DISCUSSION

3. 1. Potentiodynamic polarization

The corrosion polarization plots of untreated and heat treated MSS 420 and ASS 316 steel specimens in H_2SO_4 and HCl acid media at specific molarities are depicted in Figs. 1-4. The results obtained from the plots are presented in Tables 2-5. Table 2 shows the sharp contrast in corrosion rate values between untreated and heat treated MSS 420 steel specimens with increase in H_2SO_4 concentration. The corrosion rates for the untreated steel were significantly higher than the heat treated from 1-6M H_2SO_4 acid concentrations. This is due to the aggressive nature of its ionic species on the untreated steel and breakdown of the steel's passive film as a result of hydrogen depolarization mechanism whereby reduced hydrogen ions from the acid solution in cathodic areas become gaseous resulting causing the consistent flow of electrons and corrosion deterioration (Sadawy, 2008) The lower corrosion rates on the heat treated MSS 420 steel specimens is attributed to dispersed carbides and the presence of retained austenite and martensite formation due to the diffusion of carbon (Berns and Theisen, 2008; Fischmeister, 1988). Metallic corrosion is complex and non-homogeneous due to the presence of numerous anodic and cathodic reaction cells on its surface which are oxidized in the acid solution possibly causing the formation of porous oxides and pits as a result of the depassivation effect in iron dissolution within the alloy substrate or breakdown of passivity on the stainless steel. The increased presence of corrosive ions within the acid solution accelerated the corrosion rate causing the formation of pores and channels within the oxide layer which lead to further corrosion.

The corrosion rates for MSS 420 in Table 3 displayed similar trend with values in Table 2. The untreated steel has higher corrosion rates than the heat treated, however the values in HCl acid concentrations are generally higher the values in H_2SO_4 acid. There is a strong shift in the corrosion potential on the polarization plots for untreated MSS 420 steel specimens in H_2SO_4 and HCl acid (Figs. 1 & 2) to anodic potentials. This corresponds with anodic dissolution of the steel matrix due to corrosion as a result of the action of SO_4^{2-} and Cl- ions. The effect of the Cl- ions seems more deleterious than SO_4^{2-} due to its relatively small size and strong electronegativity which enables diffusion through the passive film on the steel surface thus accelerating the dissolution rate of the steel. Increase in acid concentration kept the potential values of the untreated specimens at anodic potentials coupled with significant increase in corrosion current. It must be noted that the presence of Cl- and SO_4^{2-} ions accelerated the redox electrochemical mechanisms responsible for corrosion, thus the capacity of the steel specimens to repair their film was drastically reduced and the protection was lost. The polarization plot for heat treated MSS 420 stainless steel in H_2SO_4 and HCl acid media shifts to noble corrosion potentials in comparison to the untreated samples. This corresponds with its low corrosion rate and high corrosion resistance as a result of the presence of the passive film which resist metal dissolution.

Polarizations results for ASS 316 untreated steel specimens in H_2SO_4 (Tables 4) shows a general decline in corrosion rate values with increase in H_2SO_4 concentration. The steel tends to be more resistant to corrosion at higher H_2SO_4 concentrations. ASS 316 heat treated steel showed strong corrosion resistance with lower corrosion rate values than the untreated steel. The corrosion rate of the heat treated steel was generally the same at all H_2SO_4 concentrations. The heat treated steel tends to be more stable in the acid solution with minimal deviation in corrosion rate values. The polarization curves for both the untreated and heat treated ASS 316 steel specimens in Fig. 3 shifts to noble values after 1M H_2SO_4, indicating strong influence of hydrogen evolution and oxygen reduction reactions in the redox electrochemical process. This is confirmed from the values of the cathodic slopes in Table 4 for the untreated and heat treated steel samples. The hydrogen atoms are assumed to diffuse through the passive films decreasing the stability of the film and hindering the repassivation process. It is

well known that passive films on most metals exhibit semiconductor or insulator characteristics (Dean and Stimming, 1989). The cathodic slopes alternate between competing values while the anodic slopes remained generally constant throughout. The useful alloying elements responsible for corrosion resistance especially chromium depletes in the surface region of the steel. The formation of Cr_2O_3 is suppressed, which is the primary reason for resistance to corrosion (Kewther *et al*., 2001).

Result for untreated and heat treated ASS 316 steel samples in HCl acid (Table 5) contrasts the values in Table 4. General observation shows that HCl acid is more corrosive at lower concentrations compared to its higher concentrations. Increase in corrosion rate was observed with increase in HCl acid concentration for the untreated steel. The heat treated steel showed a remarkable decrease in corrosion rate with increase in HCl concentration probably due to changes in the microstructure of the steel and the presence of a higher quantity of alloying elements trapped in solid solution in the alloy matrix in comparison to the untreated steel (Candelaria and Pinedo, 2003; Hidalgo, 1980). The results show that the heat treatment reduces the metal dissolution of the alloy through formation of an oxide layer at the heat treated steel surface or through stifling the removal of metallic ions via complex ion formation.

Table 2. Polarization results for untreated and heat treated MSS 420 in 1-6M H_2SO_4

Untreated MSS 420							
H_2SO_4 Conc. (M)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm^2)	Corrosion Potential (V)	Polarization Resistance (Ω)	Cathodic Tafel Slope (V/dec)	Anodic Tafel Slope (V/dec)
1M	5.62	5.79E-04	5.12E-04	-0.452	26.24	5.33	-7.88
2M	7.17	7.40E-04	6.55E-04	-0.378	47.61	4.07	-7.04
3M	8.56	8.83E-04	7.81E-04	-0.450	81.80	10.94	-8.98
4M	9.61	9.91E-04	8.77E-04	-0.360	43.48	6.66	-7.08
5M	11.60	1.20E-03	1.06E-03	-0.347	43.11	8.27	-8.07
6M	13.41	1.38E-03	1.22E-03	-0.356	32.83	7.71	-7.53
Heat Treated MSS 420							
H_2SO_4 Conc. (M)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm^2)	Corrosion Potential (V)	Polarization Resistance (Ω)	Cathodic Tafel Slope (V/dec)	Anodic Tafel Slope (V/dec)
1M	0.58	6.01E-05	5.32E-05	-0.020	98.78	13.01	-8.23
2M	1.50	1.55E-04	1.37E-04	-0.050	48.06	8.00	-6.77
3M	2.09	2.16E-04	1.91E-04	-0.042	52.90	8.03	-7.64
4M	3.06	3.16E-04	2.79E-04	-0.033	45.43	8.40	-8.09
5M	5.18	5.34E-04	4.72E-04	-0.037	27.52	7.47	-7.19
6M	6.26	6.45E-04	5.71E-04	-0.029	38.63	9.11	-7.48

Table 3. Polarization results for untreated and heat treated MSS 420 in 1-6M HCl

Untreated MSS 420							
HCl Conc. (M)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm^2)	Corrosion Potential (V)	Polarization Resistance (Ω)	Cathodic Tafel Slope (V/dec)	Anodic Tafel Slope (V/dec)
1M	11.07	1.14E-03	1.01E-03	0.071	181.80	9.51	-10.46
2M	17.64	1.82E-03	1.61E-03	-0.137	61.28	5.04	-5.91
3M	24.63	2.54E-03	2.25E-03	-0.242	10.12	2.36	-7.05
4M	30.98	3.19E-03	2.83E-03	-0.232	13.21	5.96	-6.75
5M	52.64	5.43E-03	4.80E-03	-0.373	201.00	19.91	-9.42
6M	77.32	7.97E-03	7.06E-03	0.399	26.41	11.59	-8.75
Heat Treated MSS 420							
HCl Conc. (M)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm^2)	Corrosion Potential (V)	Polarization Resistance (Ω)	Cathodic Tafel Slope (V/dec)	Anodic Tafel Slope (V/dec)
1M	1.88	1.94E-04	1.72E-04	-0.163	132.30	8.60	-7.12
2M	4.05	4.17E-04	3.69E-04	-0.106	61.58	8.15	-6.05
3M	9.33	9.62E-04	8.51E-04	-0.092	26.72	6.72	-5.43
4M	11.16	1.15E-03	1.02E-03	-0.073	39.51	8.83	-5.20
5M	14.34	1.48E-03	1.31E-03	-0.066	21.79	8.14	-6.53
6M	17.47	1.80E-03	1.59E-03	-0.058	18.34	9.49	-6.53

Table 4. Polarization results for untreated and heat treated ASS 316 in 1-6M H_2SO_4

Untreated ASS 316							
H_2SO_4 Conc. (M)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm^2)	Corrosion Potential (V)	Polarization Resistance (Ω)	Cathodic Tafel Slope (V/dec)	Anodic Tafel Slope (V/dec)
1M	15.25	2.93E-04	1.46E-03	0.243	788.90	-8.91	20.02
2M	9.33	1.79E-04	8.96E-04	-0.106	235.50	-11.19	19.12
3M	5.24	1.01E-04	5.03E-04	0.035	255.30	-12.14	21.10
4M	3.04	5.83E-05	2.92E-04	0.011	92.00	-9.25	14.40
5M	2.58	4.96E-05	2.48E-04	0.024	135.50	-9.51	17.78
6M	1.54	2.95E-05	1.47E-04	-0.220	87.16	-7.59	-2.08
Heat Treated ASS 316							
H_2SO_4 Conc. (M)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm^2)	Corrosion Potential (V)	Polarization Resistance (Ω)	Cathodic Tafel Slope (V/dec)	Anodic Tafel Slope (V/dec)
1M	6.84	1.31E-04	6.56E-04	0.080	195.80	-9.44	19.48
2M	6.35	1.22E-04	6.09E-04	-0.016	396.10	-11.89	26.59
3M	5.92	1.14E-04	5.68E-04	0.061	140.10	-12.49	11.43
4M	4.21	8.08E-05	4.04E-04	-0.036	97.39	-9.81	14.16
5M	3.69	7.09E-05	3.54E-04	0.000	263.50	-7.69	31.05
6M	4.43	8.50E-05	4.25E-04	-0.039	76.71	-8.80	11.83

Table 5. Polarization results for untreated and heat treated ASS 316 in 1-6M H_2SO_4HCl

Untreated ASS 316							
HCl Conc. (M)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm^2)	Corrosion Potential (V)	Polarization Resistance (Ω)	Cathodic Tafel Slope (V/dec)	Anodic Tafel Slope (V/dec)
1M	1.37	2.63E-05	1.32E-04	-0.173	404.80	28.84	-6.09
2M	3.26	6.25E-05	3.13E-04	-0.192	206.30	17.33	-11.29
3M	5.07	9.72E-05	4.86E-04	-0.131	655.10	44.53	-5.87
4M	7.68	1.47E-04	7.37E-04	-0.179	791.40	24.99	-11.16
5M	10.94	2.10E-04	1.05E-03	-0.380	111.70	13.19	-7.71
6M	16.18	3.10E-04	1.55E-03	-0.375	126.30	14.40	-8.77
Heat Treated ASS 316							
HCl Conc. (M)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm^2)	Corrosion Potential (V)	Polarization Resistance (Ω)	Cathodic Tafel Slope (V/dec)	Anodic Tafel Slope (V/dec)
1M	3.73	7.17E-05	3.58E-04	-0.336	1187.00	-7.71	26.35
2M	2.18	4.18E-05	2.09E-04	-0.380	358.10	-8.20	11.59
3M	1.13	2.17E-05	1.09E-04	-0.263	616.00	-9.14	32.03
4M	0.77	1.48E-05	7.40E-05	-0.255	245.20	-8.36	21.40
5M	0.51	9.80E-06	4.90E-05	-0.255	245.20	-8.36	21.40
6M	0.37	7.16E-06	3.58E-05	-0.093	339.60	-9.04	15.10

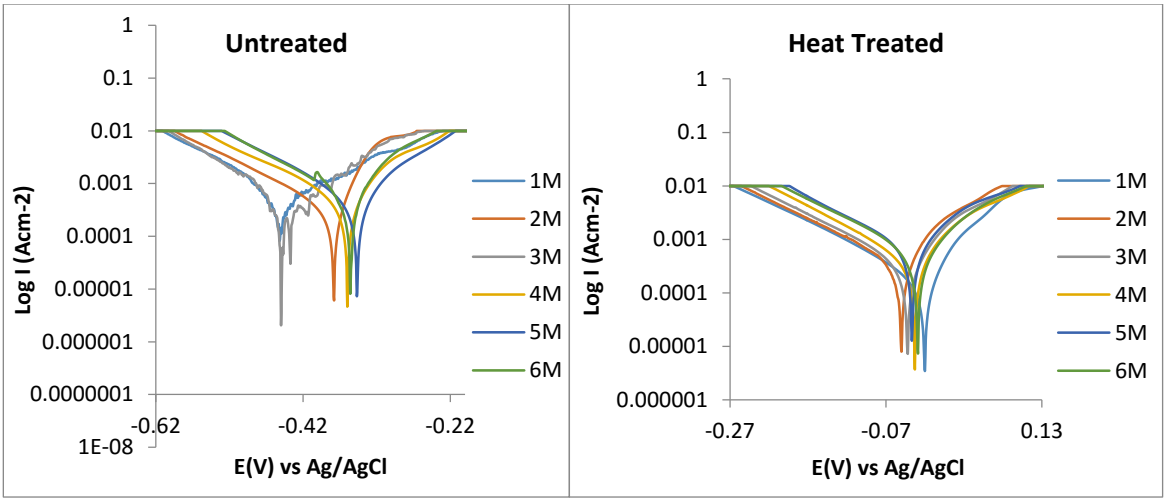

Figure 1. Polarization results for untreated and heat treated MSS 420 in 1-6M H_2SO_4

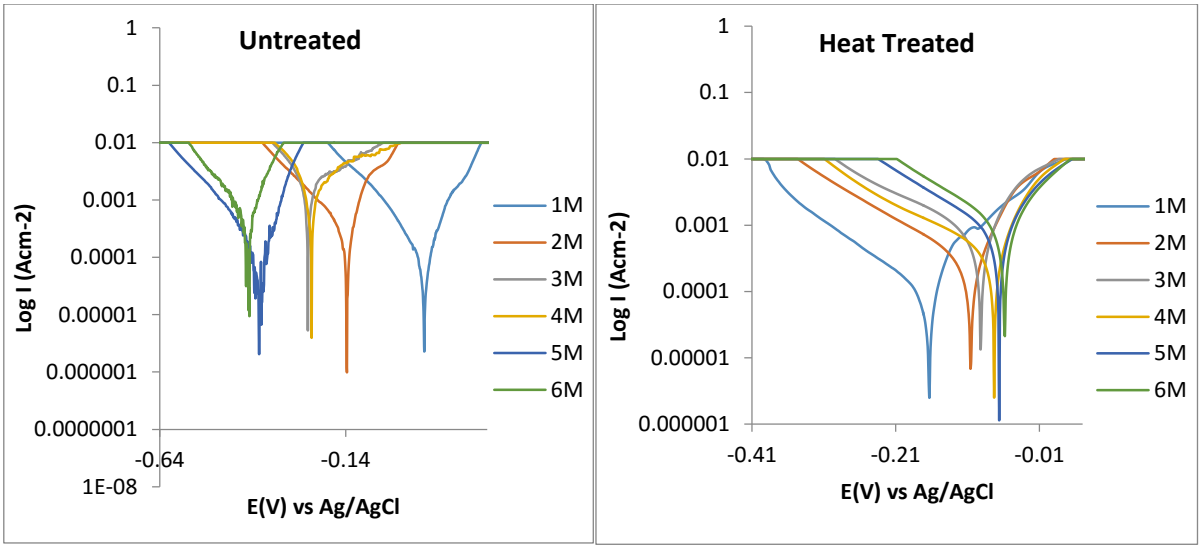

Figure 2. Polarization results for untreated and heat treated MSS 420 in 1-6M HCl

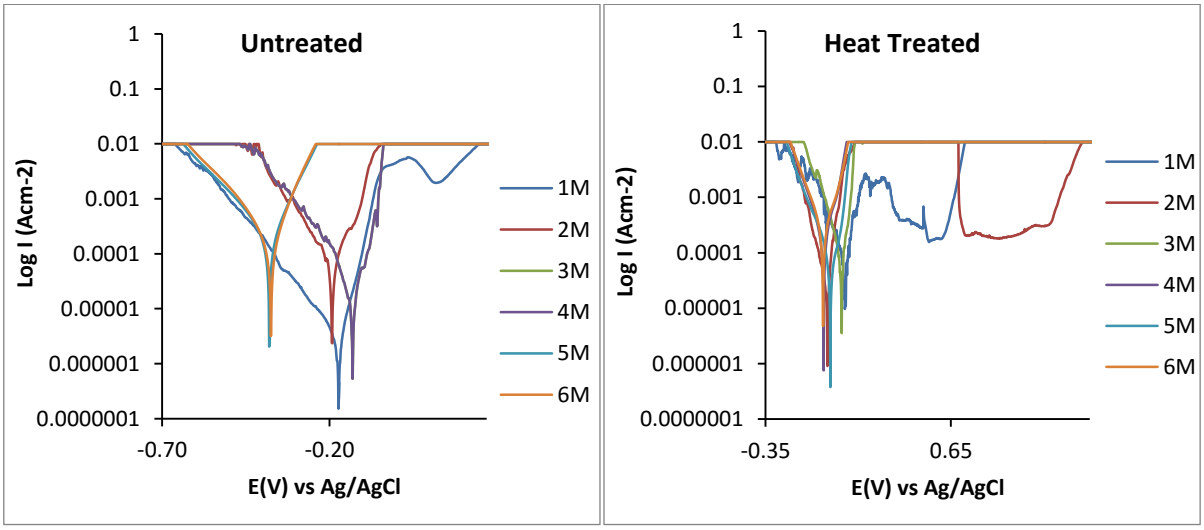

Figure 3. Polarization results for untreated and heat treated ASS 316 in 1-6M H_2SO_4

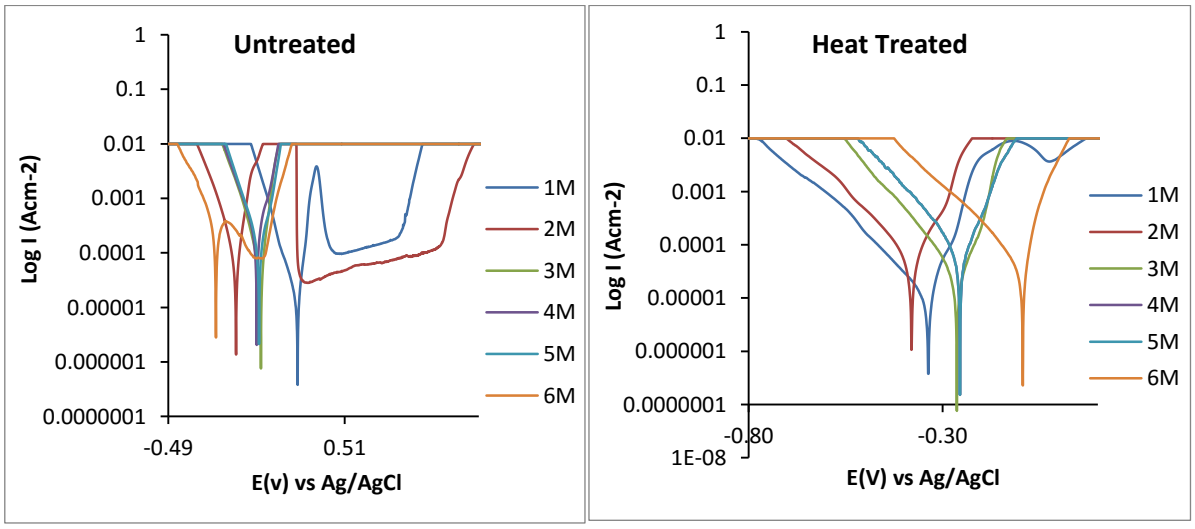

Figure 4. Polarization results for untreated and heat treated ASS 316 in 1-6M HCl

3. 2. Coupon analysis

Results for weight loss ($\tilde{\omega}$) and corrosion rate (γ) for MSS 420 and ASS 316 in H_2SO_4 and HCl acid media are presented in Tables 6 & 7. Figs. 5-8 show the plots of corrosion rate versus exposure time in the acid media for both steel specimens. The untreated MSS 420 and ASS 316 specimens corroded significantly in comparison to the heat treated steel specimens. The steel reacts spontaneously in both acids due to redox electrochemical reactions which results in the release of Fe^{2+} ions into the acid solutions. Observation of Table 6 shows a gradual increase in corrosion rate for MSS 420 specimens with increase in H_2SO_4 and HCl acid concentration (1-6M) for the untreated and heat treated steel specimens; however the corrosion rate for the heat treated specimens are generally lower than values for the heat treated while the values in H_2SO_4 are generally lower than values in HCl acid media. Corrosion rate values for ASS 316 (untreated and heat treated steel specimens) in Table 7 are significantly higher in both acids when compared to values for MSS 420 specimens (Table 6). The values for untreated ASS 316 decreased significantly with increase in H_2SO_4 acid concentration. This contrast corrosion rate values in HCl acid where the corrosion rate increased with increase in HCl acid concentration.

The corrosion behavior of the steel specimens during the exposure hours are clearly shown in the Figures earlier mentioned (Figs. 5-8). It can be seen in Fig. 5 that heat treatment significantly increases the corrosion resistance of MSS 420 in H_2SO_4 acid media whereby the corrosion rate remained generally constant and at very low values. Heat treatment has limited effect on the corrosion resistance of the steel in HCl (Fig. 6). The plot of corrosion rate versus exposure time (Fig. 7) for ASS 316 in H_2SO_4 shows that heat treatment slightly improves its corrosion resistance however changes in H_2SO_4 concentration (1-6M) has no influence on its corrosion rate values. In HCl (Fig. 8) heat treatment improves the corrosion resistance of ASS 316 however the overall effect is insignificant as the change in corrosion rate is negligible. The aggressive nature of the HCl acid solution is due to the presence of chloride ions. Chloride ions diffuses through the passive protective films of steel specimens and upon reaching the metal/film interface, results in film breakdown [44-48]. MSS 420 specimens show higher resistance to electrochemical deterioration from chloride ions.

Comparative analysis of heat treatment on the corrosion resistance of MSS 420 and ASS 316 specimens are shown in Fig. 9 and 10. Heat treatment has a strong influence on the surface properties and corrosion resistance of MSS 420 specimen most especially in H_2SO_4 acid media were the corrosion rates reduced significantly. The effect of heat treatment on ASS 316 specimen is limited as the corrosion rates were not significantly altered however the corrosion rates of the heat treated steel is lower. The results show that heat treated improves to an extent the corrosion rates of the steel specimens.

Table 6. Results for MSS 420 specimens in dilute H_2SO_4 and HCl acid media from weight loss analysis

	Untreated (H_2SO_4)		Heat Treated (H_2SO_4)			Untreated (HCl)		Heat Treated (HCl)		
Acid Conc. (M)	Weight Loss (g)	Corrosion Rate (mm/y)	Weight Loss (g)	Corrosion Rate (mm/y)	Percentage Improvement (Corrosion Rate) %	Weight Loss (g)	Corrosion Rate (mm/y)	Weight Loss (g)	Corrosion Rate (mm/y)	Percentage Improvement (Corrosion Rate) %
1M	0.248	0.353	0.091	0.129	63.3	0.214	0.304	0.117	0.166	45.6
2M	0.184	0.262	0.092	0.130	50.3	0.761	1.082	0.212	0.301	72.1
3M	0.254	0.362	0.108	0.153	57.7	1.054	1.499	0.479	0.682	54.5
4M	0.305	0.433	0.113	0.160	63.0	2.240	3.185	0.727	1.034	67.5
5M	0.393	0.559	0.129	0.183	67.2	2.289	3.255	1.325	1.884	42.1
6M	0.411	0.584	0.122	0.173	70.4	3.448	4.903	1.530	2.175	55.6

Table 7. Results for ASS 316 specimens in dilute H_2SO_4 and HCl acid media from weight loss analysis

	Untreated (H_2SO_4)		Heat Treated (H_2SO_4)			Untreated (HCl)		Heat Treated (HCl)		
Acid Conc. (M)	Weight Loss (g)	Corrosion Rate (mm/y)	Weight Loss (g)	Corrosion Rate (mm/y)	Percentage Improvement (Corrosion Rate) %	Weight Loss (g)	Corrosion Rate (mm/y)	Weight Loss (g)	Corrosion Rate (mm/y)	Percentage Improvement (Corrosion Rate) %
1M	0.135	200.461	0.028	40.956	79.6	0.053	78.636	0.042	62.402	20.6
2M	0.056	83.401	0.033	38.551	53.8	0.072	107.379	0.051	70.955	33.9
3M	0.033	48.998	0.016	34.276	30.0	0.114	170.079	0.094	125.293	26.3
4M	0.022	33.063	0.019	28.148	14.9	0.240	357.434	0.191	224.756	37.1
5M	0.016	32.829	0.021	31.276	4.7	0.388	578.001	0.327	406.706	29.6
6M	0.021	31.722	0.024	30.999	2.3	0.638	950.329	0.486	683.805	28.0

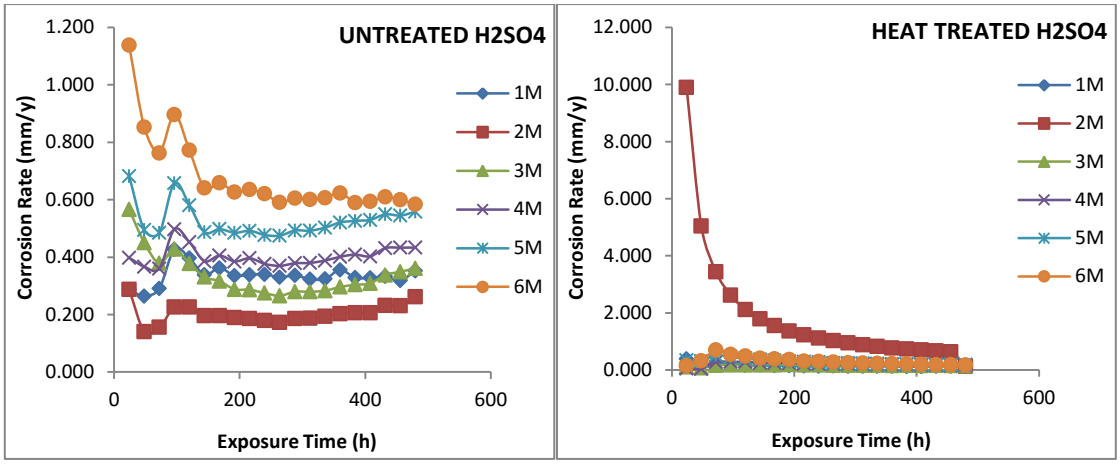

Figure 5. Plot of corrosion rate versus exposure time for MSS 420 specimen in H_2SO_4 acid media

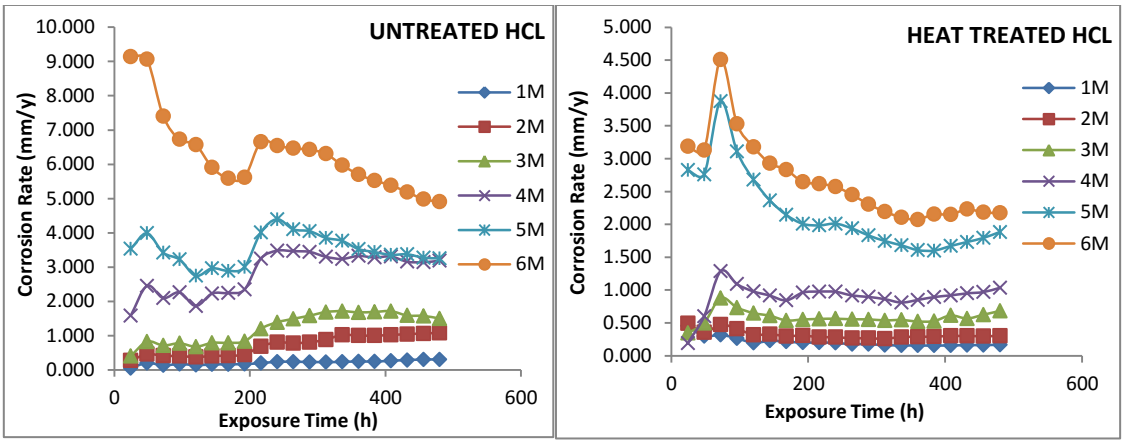

Figure 6. Plot of corrosion rate versus exposure time for MSS 420 specimen in HCl acid media

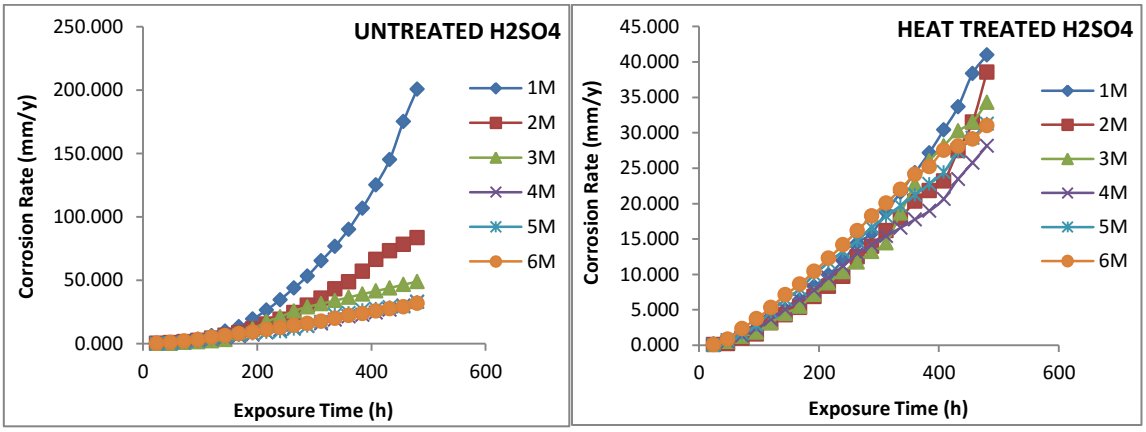

Figure 7. Plot of corrosion rate versus exposure time for ASS 316 specimen in H_2SO_4 acid media

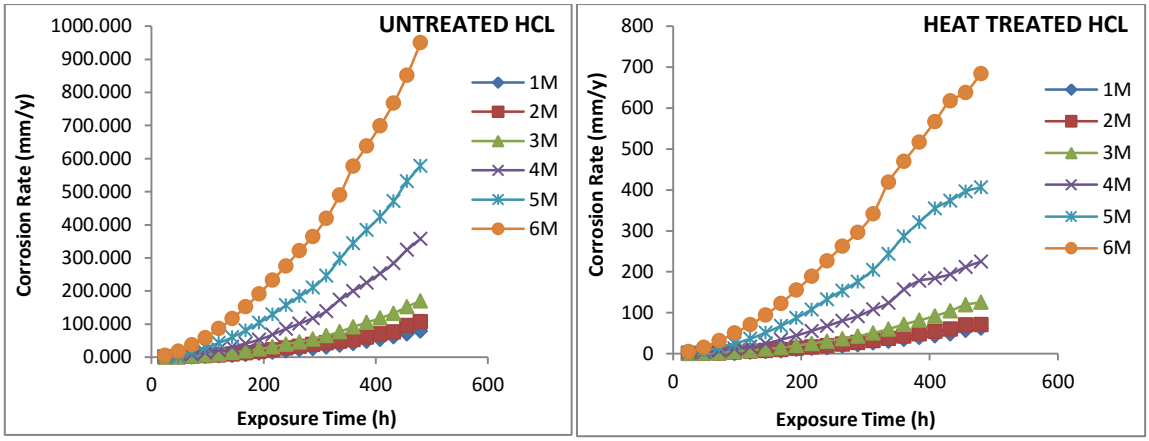

Figure 8. Plot of corrosion rate versus exposure time for ASS 316 specimen in HCl acid media

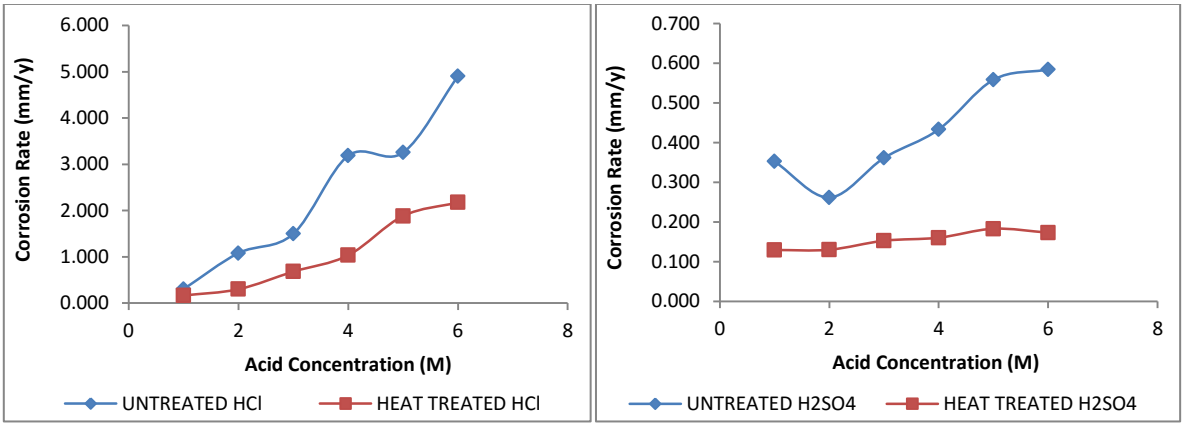

Figure 9. Comparative plot of untreated and heat treated MSS 420 in H_2SO_4 and HCl acid media

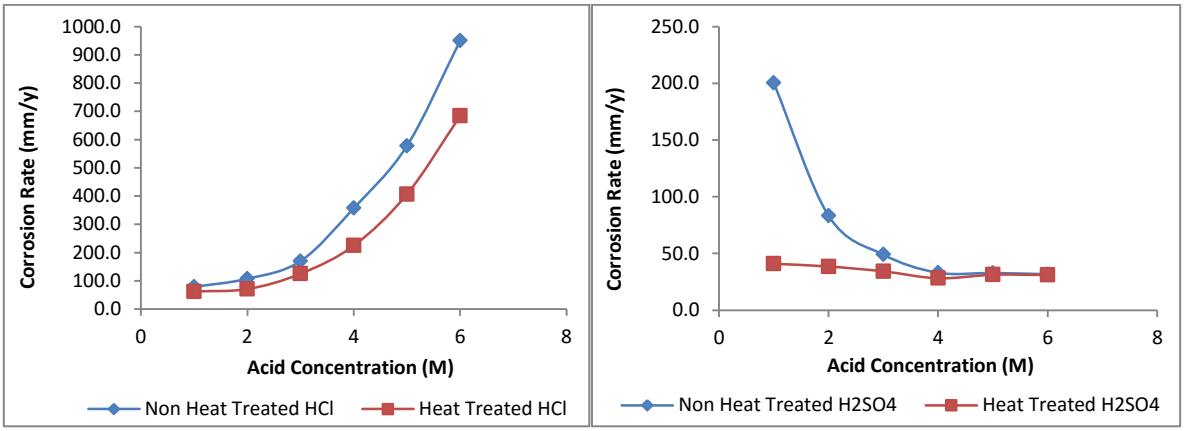

Figure 10. Comparative plot of untreated and heat treated ASS 316 in H_2SO_4 and HCl acid media

3.3 Optical Microscopy

The optical microscopy images of MSS 420 and ASS 316 specimens are shown from Fig. 11 - Fig. 16 at magnification of x40. Fig. 11 shows the images of MSS 420 as received and after heat treatment. The heat treated steel has a darker morphology due to greater concentration of carbides and transformation of the metallurgical properties resulting in the presence of retained austenite as earlier discussed. The image of the untreated and heat treated MSS 420 after weight loss measurement in H_2SO_4 and HCl acid solution are

presented in Figs. 12 & 13. The effect of heat treatment is clearly visible on the surface morphology of the steel specimens after the corrosion test. The untreated steel showed severe corrosion and deterioration of the surface properties of the steel while the heat treated steel confirms strong corrosion resistance. These observations confirm the result from weight loss and potentiodynamic polarization test. Fig. 14 shows the image of the as received and heat treated ASS 316 specimens before corrosion test. Figs. 15 & 16 show the image of the untreated and heat treated ASS 316 specimens after the corrosion test from H_2SO_4 and HCl acid solution. The heat treatment effect on the corrosion resistance of the steel is minimal most especially for the specimen from HCl solution. Surface deterioration is due to corrosion from anions of SO_4^{2-} and Cl^- within the acid solution. The steel is unacceptable for applications in very corrosive environments as rapid deterioration occurs.

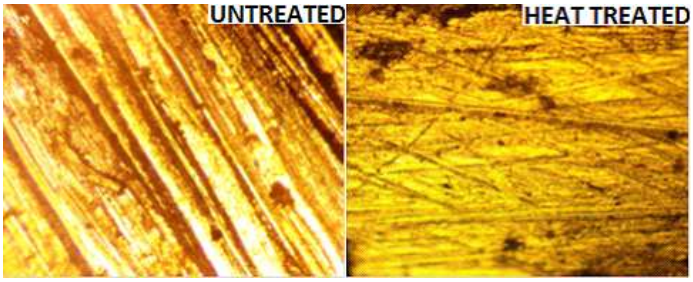

Figure 11. Micrographs of untreated and heat treated MSS steel samples before corrosion test

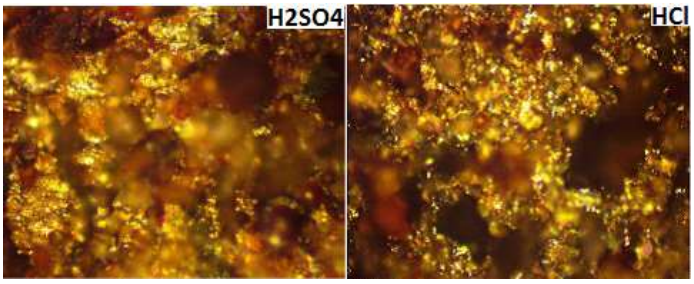

Figure 12. Micrographs of untreated MSS steel samples in H_2SO_4 and HCl after 480hrs

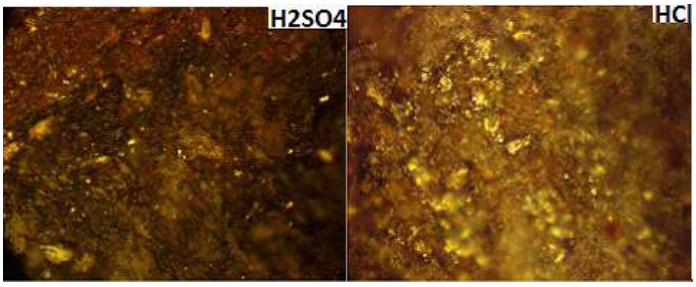

Figure 13. Micrographs of heat treated steel samples in H_2SO_4 and HCl after 480hrs

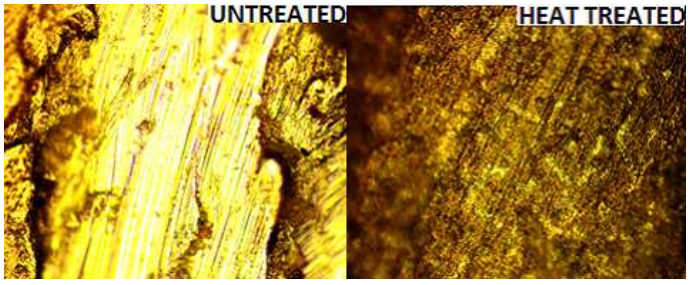

Figure 14. Micrographs of untreated and heat treated ASS steel samples before corrosion test

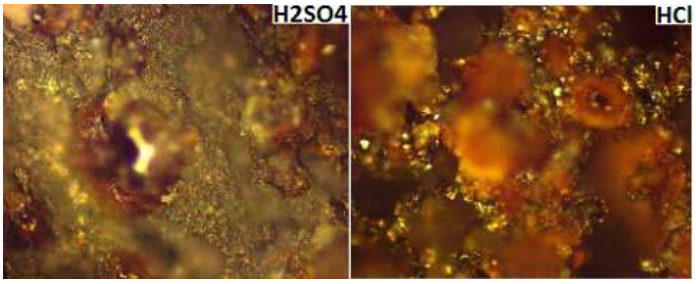

Figure 15. Micrographs of untreated ASS steel samples in H_2SO_4 and HCl after 480hrs

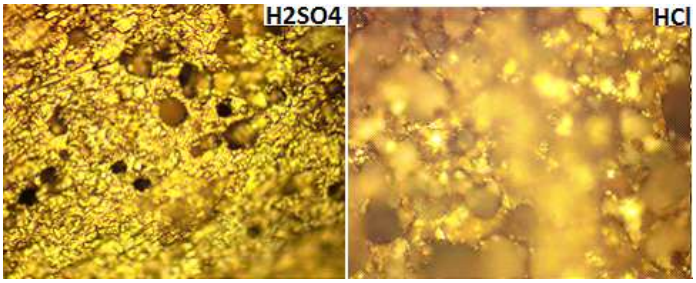

Figure 16. Micrographs of heat treated ASS steel samples in H_2SO_4 and HCl after 480hrs

4. CONCLUSION

This The corrosion resistance of 420 martensitic stainless steel increased significantly after quenching heat treatment due to the presence of retained austenite and martensitic transformation which produced a hardened surface and more resilient passivation characteristics. The percentage improvement in corrosion rate in the acid media used was 59.1% as compared to the annealed heat treated 316 austenitic stainless steel at 30.1% whose increase in corrosion resistance was negligible as heat treatment did not result in any positive change in its corrosion resistance characteristics. The corrosion rate of 316 stainless steel was relatively higher than the 420 stainless steel. Optical microscopy characterization for heat treated 316 stainless steel showed a badly corroded morphology. The microscopy image for heat treated 420 stainless steel showed a corrosion resistant surface, confirming the results obtained from coupon analysis and potentiodynamic polarization test.

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REFERENCES

Ahmad K (2006) “Principles of corrosion engineering and corrosion control”, Butterworth-Heinemann, Oxford, UK.

Aponte B, Romero MF, Rincón TO, Arias S, Contreras M, Ramo J, Collantes R (2008) “Corrosion costs in preventive and corrective maintenance in equipment and facilities in industry” *Revista Técnica de la Facultad de Ingeniería Universidad del Zulia*, 31, pp. 87-96.

ASTM G1 - 03(2011), Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. http://www.astm.org/Standards/G1[Retrieved: 30/05/2016].

ASTM G102 - 89(2015)e1. Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements. http://www.astm.org/Standards/G31 [Retrieved: 30/05/2016].

ASTM G59 - 97(2014). Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements. http://www.astm.org/Standards/G31[Retrieved: 30/05/2016].

ASTM NACE / ASTMG31 - 12a (2012), Standard Guide for Laboratory Immersion Corrosion Testing of Metals. http://www.astm.org/Standards/G31[Retrieved: 30/05/2016].

Berns H, Theisen W (2008) “Ferrous materials—steel and cast iron”, 1st edn., Springer Verlag Berlin, Heidelberg, New York.

Betova I, Bojinov M, Kinnunen P, Pohjanne P, Saario T (2002) “Influence of the electrolyte composition and temperature on the transpassive dissolution of austenitic stainless steels in simulated bleaching solutions”, *Electrochimica Acta*, 47, pp. 3335 - 3349.

Brickner KG (1968) “Stainless steel for room and cryogenic temperatures”, *Metals Engineering Quarterly*, pp. 25-45.

Candelaria AF, Pinedo CE (2003) “Influence of the heat treatment on the corrosion resistance of the martensitic stainless steel type AISI 420”, *Journal of Materials Science Letters*, 22(16), pp. 1151-1153.

Choi YS, Kim JG, Park YS, Park JY (2007) “Austenitizing treatment influence on the electrochemical corrosion behavior of 0.3C–14Cr–3Mo martensitic stainless steel”, *Materials Letters*, 61(1), pp. 244–47.

Dean MH, Stimming U (1989) “The electronic properties of disordered passive films”, *Corrosion Science*, 29(2-3), pp. 199-211.

Dell KA (1989) “Metallurgy Theory and Practical Textbook,” American Technical Society, Chicago.

Dong J, Zhou J (2000) “An investigation of pitting initiation mechanism of Cr12Ni2W1Mo1V steel after induction hardening”, *Journal of Material Science*, 35(11), pp. 2653-2657.

Fadare DA, Fadara G (2013) “Corrosion resistance of heat-treated NST 37-2 steel in hydrochloric acid solution”, *Journal of Minerals and Materials Characterization and Engineering*, 1, pp. 1-7.

Fischmeister HF, Karagoz S, Andern H (1988) “An atom probe study of secondary hardening in high speed steels”, *Acta Metallurgical Materials*, 36, pp. 817-825.

Gaudett MA, Scully JR (1994) “Applicability of bond percolation theory to intergranular stress-corrosion cracking of sensitized AlSl 304 stainless steel”, *Metallurgical and Materials Transaction A*, 25A(4), pp.775-787.

Hidalgo PJ (1980) “Pitting corrosion of martensitic cutlery steels”, Surface Technology, 10(3), pp. 193-208.

Kempester MHA (1984) “Materials for Engineers”, 3rd ed., Hoodder and Stonghton, London.

Kewther A, Yilbas BS, Hashmi MSJ (2001) “Corrosion properties of inconel 617 alloy after heat treatment at elevated temperature”, *Journal of Materials Engineering and Performance*, 10(1), pp.108-113.

Khatak HS, Baldev R (2002) “Corrosion of Austenitic Stainless Steels: Mechanism, Mitigation and Monitoring; ASM International”, Narosa Publishing House.

Lu S, Chen Y, Yao K, Ge X “Influence of heat treatment on microstructure evolution, surface roughness and corrosion resistance of a martensitic stainless steel”, *Transactions of Materials and Heat Treatment*, 36, pp. 223-229, 2015

Lu S, Yao K, Chen Y, Wang M, Ge X (2015) “Influence of heat treatment on the microstructure and corrosion resistance of 13 Wt %Cr-Type martensitic stainless steel”, *Metallurgical and Materials Transactions A*, 46A, pp. 6090-6102.

Marshall P (1984) “Austenitic Stainless Steels: Microstructure and Mechanical Properties”, Elsevier Applied Science Publishers Ltd, New York.

Millano V, Sanchez M, Rincon OT, Linares D, Romero N (2006) “Electrochemical behavior study of AISI 304 and 316 in carbonate or chloride contaminated concrete”, *Revista Técnica de la Facultad de Ingeniería Universidad del Zulia*, 29(3), pp. 291-298.

Moussa MHN, El-Far AA, El-Shafei AA (2007) “The use of water-soluble hydrazones as inhibitors for the corrosion of C-steel in acidic medium”, *Materials Chemistry and Physics*, 105, pp. 105-113.

Nasery IA, Saghafiana H, Borhanib G (2011) “The effect of heat treatment on mechanical properties and corrosion behavior of AISI420 martensitic stainless steel”, *Journal of Alloys and Compounds*, 509, pp. 3931-3936.

Oberndorfer M, Kaestenbauer M, Thayer K (2004) “Application Limits of Stainless Steels in the Petroleum. Industry”, *Materials and Corrosion*, 55, pp. 174-180.

Palit GC, Kain V, Gadiyar HS (1993) “Electrochemical investigations of pitting corrosion in nitrogen-bearing type 316ln stainless steel”, *Corrosion*, 49(12), pp. 977-991.

Rajan A (1998) “Heat treatment principles and techniques”, Prentice Hall of India, New Delhi, pp. 1-6.

Raymond A, Higgins B (1985) “Properties of Engineering Materials,” Hoodder and Stonghton, London.

Sadawy MM (2008) "Investigation of alloying elements and nonmetallic inclusions effects on the corrosion and electrochemical behavior of high alloying steel," *Journal of Al Azhar University Engineering Sector JAUES*, 3(9), pp. 1143-114.

Sethi T, Chaturvedi A, Mathur RK (2007) “Corrosion inhibitory effects of some schiff's bases on mild steel in acid media”, *Journal of Chilean Chemical Society*, 52(3), pp. 1206 (2007).

Stimming U (1986) “Photoelectrochemical studies of passive films”, *Electrochimica Acta*, 31(4), pp. 415-429.

Strehblow HH, Marcus P, Oudar J (1995) “Corrosion Mechanisms in Theory and Practice”, Marcel Dekker, New York, p. 265.